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Patentanmeldung Nr.

Patent application No. Demande de brevet nº

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PRIORITY

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A process for the removal of SO2, HCN and H2S and optionally COS, CS2 and NH3 from a gas stream

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A PROCESS FOR THE REMOVAL OF  $SO_2$ , HCN AND  $H_2S$  AND OPTIONALLY COS,  $CS_2$  AND  $NH_3$  FROM A GAS STREAM

#### FIELD OF THE INVENTION

The invention relates to a process for removing  $SO_2$ , HCN and  $H_2S$  and optionally COS,  $CS_2$  and  $NH_3$  from a gas stream.

### 5 BACKGROUND OF THE INVENTION

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The removal of sulphur compounds such as  $SO_2$  and  $H_2S$  from a gas stream comprising these compounds is of considerable importance, because the toxicity and smell of sulphur compounds renders their presence highly undesirable.

Gas streams from industrial chemical processes may contain a variety of sulphur compounds such as  $H_2S$ ,  $SO_2$ ,  $CS_2$  and COS. In addition, other compounds whose presence is undesirable may be present such as HCN or  $NH_3$ . It is often necessary for the intended purposes of the gas stream to remove these compounds at least partly, for example to prevent catalyst poisoning in processes after the gasification stage.

Processes for the removal of sulphur compounds are known in the art. In EP 324,526 a process is described for the removal of H<sub>2</sub>S, COS, CS<sub>2</sub> and SO<sub>2</sub> from a gas stream, by converting COS and CS<sub>2</sub> into H<sub>2</sub>S. Although EP 324,526 mentions that the removal of H<sub>2</sub>S can be achieved, it does not specify the preferred type of process for H<sub>2</sub>S removal, nor is the concentration of H<sub>2</sub>S in the treated gas stream mentioned.

A process known in the art for the removal of  $\rm H_2S$  from a gas stream is the partial oxidation of  $\rm H_2S$  to  $\rm SO_2$  according to:

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(1) Partial  $H_2S$  oxidation  $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$ The SO<sub>2</sub> formed can be (catalytically) converted to elemental sulphur according to the Claus reaction: (2) Claus reaction  $4H_2S + 2SO_2 \iff 4H_2O + 3S_2$ This process is known as the Claus process. The Claus process is frequently employed both in refineries and for the processing of H2S recovered from natural gas. A disadvantage of the Claus process is that it is thermodynamically limited by the increase of the water vapour content and simultaneously by the decrease of the  ${\rm H_2S}$  and  ${\rm SO_2}$  concentration as the  ${\rm H_2S}$  conversion proceeds, with the result that the equilibrium of the Claus reaction shifts to the left. Since the dew point of water lies below the solidification point of sulphur, condensation of the water vapour in the process gas to remove this limitation can lead to serious problems, such as clogging due to the solidification of sulphur and corrosion due to the formation of sulfuric acid, causing

serious operational problems.

Another disadvantage of the Claus process is that the concentration of H<sub>2</sub>S in the treated gas is still relatively high. The Claus process has been improved to an extent where the H<sub>2</sub>S content of the treated gas can be lowered to approximately 1 vol% (Superclaus-99 process) and the SO<sub>2</sub> content to approximately 0.02 vol%. However, especially in the case where it is necessary to comply with requirements with regard to residential use or environmental regulations with respect to emission of sulphur compounds, even lower concentrations of H<sub>2</sub>S and

 ${\rm SO}_2$ , in the ppm range, have to be achieved. A disadvantage of the Claus and Superclaus process is that such low concentrations of  ${\rm H}_2{\rm S}$  and  ${\rm SO}_2$  cannot be achieved.

The removal of HCN from gas streams is important not only because of its own toxic properties, but also in view of corrosive NO<sub>X</sub> compounds which can evolve when both HCN and oxygen are present in a gas stream. In addition, HCN itself is corrosive to equipment when allowed to concentrate in liquid streams upon gas treating.

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We have now found a relatively simple and inexpensive process for removing SO<sub>2</sub>, H<sub>2</sub>S and HCN and optionally COS, CS<sub>2</sub> and NH<sub>3</sub> from a gas stream. In the process according to the invention, a combination of reaction steps is used to achieve the removal of sulphur compounds such as H<sub>2</sub>S and SO<sub>2</sub>, and optionally also COS and/or CS<sub>2</sub>, as well as HCN from a gas stream comprising these compounds, to concentrations of below 10 ppmv for H<sub>2</sub>S, below 100 ppmv for SO<sub>2</sub> and below 0.01 vol%, preferably 10 ppmv for HCN.

Another advantage of the process according to the invention compared to the Claus process is that it is not necessary to produce a gas with a high H<sub>2</sub>S content, for example by amine treatment, prior to H<sub>2</sub>S removal. In the Claus process, a pretreatment to produce a gas with a high H<sub>2</sub>S content is necessary to make the gas suitable as a Claus feed.

Yet another advantage of the process according to the invention is that the problem of sulphur clogging —as observed in other liquid based sulphur recovery processes— is substantially less or absent due to the hydrophilic nature of the sulphur formed.

#### SUMMARY OF THE INVENTION

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The invention relates to a process for the removal of  $SO_2$ , HCN and  $H_2S$  and optionally one or more compounds from the group of COS,  $CS_2$  and  $NH_3$  from a first gas stream, which process comprises the steps of:

- (a) removing SO<sub>2</sub> from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;
- (b) removing HCN and optionally COS and/or CS2 from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;
- (c) removing NH<sub>3</sub> from the third gas stream by contacting the third gas stream in a NH<sub>3</sub>-removal zone with an aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream;
- (d) removing H<sub>2</sub>S from the fourth gas stream by contacting the fourth gas stream in a H<sub>2</sub>S-removal zone with an aqueous alkaline washing liquid to obtain a H<sub>2</sub>Sdepleted gas stream and a hydrogen-sulphide-comprising aqueous stream;
- (e) contacting the hydrogen-sulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in a oxidation reactor to obtain a sulphur slurry and a regenerated aqueous alkaline washing liquid;
- (f) separating at least part of the sulphur slurry 30 obtained in step (e) from the regenerated aqueous alkaline washing liquid and;

(g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the  ${\rm H_2S\text{--}removal}$  zone in step (d).

## DETAILED DESCRIPTION OF THE INVENTION

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In step (a) of the process according to the invention, SO<sub>2</sub> is removed from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream. In the hydrogenation zone, SO<sub>2</sub> is converted to H<sub>2</sub>S according to reaction (3):

(3) Hydrogenation reaction  $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$ 

Reference herein to a first gas stream is to a gas stream comprising  $H_2S$ ,  $SO_2$ , HCN and optionally COS,  $CS_2$  and  $NH_3$  or combinations thereof. The total concentration of sulphur compounds in the first gas stream is suitably between 10 ppmv and 30 vol%, preferably between 100 ppmv and 20 vol%, based on the total gas stream. The total concentration of HCN in the first gas stream is typically between 10 and 5000 ppmv, suitably between 20 and 1000 ppmv, or between 40 and 250 ppmv, based on the total gas stream.

Suitably, the load of sulphur compounds in the hydrogenation zone is between 50 and 50000 kg/day.

Optionally, solid compounds present in the first gas stream can be removed from the first gas stream prior to entering the hydrogenation zone, for example by use of a filter.

The hydrogenation zone can be a gas/solid contactor, preferably a fixed bed reactor. Suitable hydrogenation catalysts are for example cobalt/molybdenum or nickel/molybdenum catalysts. The hydrogenation catalysts suitable for the process according to the invention can

be supported, preferably on a refractory oxide support, more preferably on an alumina support.

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Suitably, the temperature in the hydrogenation zone is between 200 °C and 380 °C, preferably between 210 °C and 330 °C, more preferably between between 250 °C and 350 °C. The pressure in the hydrogenation zone is suitably between 1 and 100 bara, preferably between 2 and 80 bara.

Reference herein to a second gas stream is to a gas stream wherein the concentration of SO<sub>2</sub> is below 100 ppmv, preferably between 0.001 ppmv and 100 ppmv, more preferably between 0.01 ppmv and 50 ppmv, suitably between 0.1 ppmv and 15 ppmv, especially between 0.5 ppmv and 10 ppmv, based on the total gas stream.

In step (b) of the process according to the invention, HCN and optionally COS and/or CS<sub>2</sub> are removed from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream.

In the hydrolysis zone, HCN and, if applicable, COS and/or  $\text{CS}_2$  are converted according to the following reactions:

- (4) Hydrolysis of HCN:  $HCN + H_2O \rightarrow NH_3 + CO$
- (5) Hydrolysis of COS:  $COS + H_2O \rightarrow H_2S + CO_2$
- (6) Hydrolysis of CS<sub>2</sub>:  $CS_2 + 2H_2O \rightarrow 2H_2S + CO_2$

The amount of water/steam in the hydrolysis zone is preferably between 10 v/v% and 80 v/v%. Optionally, water or steam of a mixture thereof may be added to the second gas stream prior to contacting the second gas stream with the hydrogenation catalyst. Preferably, the amount of water/steam added is such that the water/steam content of the first gas stream is between 10 v/v% and 80 v/v%, preferably between 20 v/v% and 70 v/v%, more preferably

between 30 v/v% and 50 v/v%, based on steam. Typically, the reaction conditions are selected in such a way, that the reaction mixture remains below the dewpoint of  $\rm H_2O$ .

If COS and/or  $CS_2$  are present, the total concentration of COS and  $CS_2$  in the second gas stream is suitably between 10 ppmv and 2 vol\*, preferably between 20 ppmv and 1 vol\*, based on the total gas stream.

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The hydrolysis zone can be a gas/solid contactor, preferably a fixed bed reactor. Catalysts for the hydrolysis of HCN and optionally COS and/or  $CS_2$  are known to those skilled in the art and include for example  $TiO_2$ -based catalysts or catalysts based on alumina and/or chromium-oxide. Preferred catalysts are  $TiO_2$ -based catalysts.

Optionally, the hydrolysis step can be done prior to the hydrogenation step. A disadvantage of performing the hydrogenation step prior to the hydrolysis step is that when a TiO<sub>2</sub> catalyst is used, the TiO<sub>2</sub> catalyst can also catalyze the Claus reaction, leading to the formation of sulphur from H<sub>2</sub>S and SO<sub>2</sub>. However, in the case where the temperature is above the dew point of sulphur, the formation of sulphur from the Claus reaction does not lead to clogging.

Reference herein to a third gas stream is to a gas stream wherein the concentration of HCN is below 0.01 vol%, suitably between 0.1 ppmv and 0.01 vol%, preferably between 1 ppmv and 50 ppmv, based on the total gas stream.

The concentration of COS, if present, in the third gas stream is below 0.01 vol%, suitably between 10 ppmv and 0.01 vol%, preferably between 15 ppmv and 100 ppmv, based on the total gas stream.

The concentration of  $CS_2$ , if present, in the third gas stream is below 0.01 vol%, suitably between 1 ppmv and 0.01 vol%, preferably between 2 ppmv and 50 ppmv.

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An advantage of the process according to the invention is that the third gas stream obtained after the catalytic hydrogenation (step a) and the hydrolysis (step b) can be treated directly with an aqueous alkaline washing liquid followed by contacting the alkaline hydrogensulphide containing washing liquid with sulphide-oxidizing bacteria in the presence of oxygen to obtain a sulphur slurry. For other processes such as the Claus process it is necessary that first by amine treatment and regeneration a sour gas is produced that has a high H<sub>2</sub>S content to make it suitable as a Claus feed.

In step (c) of the process according to the invention NH<sub>3</sub> is removed from the third gas stream by contacting the third gas stream in an NH<sub>3</sub>-removal zone with an aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream. The amount of NH<sub>3</sub> is suitably between 10 and 6000 ppmv, preferably between 20 and 2000 ppmv. The temperature in the NH<sub>3</sub>-removal zone is suitably between 5 and 70 °C, preferably between 10 and 50 °C. The pressure in the NH<sub>3</sub>-removal zone is suitably between 1 and 100 bara, preferably between 2 and 80 bara.

In step (d) of the process according to the invention  $H_2S$  is removed from the fourth gas stream by contacting the fourth gas stream in  $H_2S$ -removal zone with an aqueous alkaline washing liquid to obtain a  $H_2S$ -depleted gas stream and a hydrogen-sulphide-comprising aqueous stream.

Suitably, the load of sulphur compounds in the  ${\rm H}_2{\rm S-removal}$  zone is below 60000 kg/day, or between 50 and

50000 kg/day, preferably between 75 and 20000 kg/day, more preferably between 100 and 10000 kg/day.

Suitably, the total amount of  $H_2S$  of the fourth gas stream is between 10 ppmv and 20 vol%, preferably between 20 ppmv and 10 vol%.

Suitable aqueous washing liquids include aqueous hydroxide solutions, e.g. sodium hydroxide or potassium hydroxide solutions in water. The pH of the aqueous alkaline solvents is suitably between 7 and 12, preferably between 8 and 11.

The main reactions that can take place in the  ${\rm H}_2{\rm S}-$  removal zone in step (d) are:

(7) H <sub>2</sub> S absorption	H <sub>2</sub> S + OH-	$\rightarrow$	HS + H20
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(8) 
$$H_2S$$
 absorption  $H_2S + CO_3^{2-} \rightarrow HS^- + HCO_3^-$ 

15 (9) 
$$CO_2$$
 absorption  $CO_2 + OH^- \rightarrow HCO_3^-$ 

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(10) Carbonate formation 
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

(11) Poly-hydrosulphide 
$$2HS^- + S_8 \rightarrow 2HS_5^-$$
 formation

The term sulphide-comprising aqueous stream as used herein refers to an aqueous stream comprising one or more products of the main reactions (7) to (11) that can take place in the H<sub>2</sub>S-removal zone, such as HS<sup>-</sup>, disulphides, polysulphides, thiocarbonates and carbonates but can also include dissolved H<sub>2</sub>S.

Due to their odorous nature, H<sub>2</sub>S, mercaptans, sulphides, disulphides and aromatic mercaptans can be detected at parts per million concentrations. Thus, it is desirable for users of such gas and refinery streams to have total concentration of sulphur compounds, especially H<sub>2</sub>S, lowered to a concentration of e.g. less than 30 or

20 ppmv, preferably less than 10 ppmv, based on the total  ${\rm H}_2{\rm S}\text{-depleted}$  gas stream.

Reference herein to " $H_2S$ -depleted gas stream" is to a gas stream wherein the total concentration of sulphur compounds, especially  $H_2S$ , is below 30 ppmv, suitably between 0.01 and 30 ppmv, or below 20 ppmv, suitably between 0.01 and 20 ppmv, or below 10 ppmv, suitably between 0.01 and 10 ppmv, preferably between 0.05 and 3.5 ppmv, more preferably between 0.1 and 1 ppmv, based on the total gas stream.

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The preferred temperature in the  $\rm H_2S$  removal zone is between 5 and 70 °C, more preferably between 10 and 50 °C. Preferably, the pressure in the  $\rm H_2S$  removal zone is between 1 and 100 bara, more preferably between 2 and 80 bara.

Typically, the H<sub>2</sub>S removal zone is a gas/liquid contactor. Suitable gas/liquid contactors are described in Perry's Chemical Engineers' Handbook, 7<sup>th</sup> edition, section 14 (1997) and include for example a tray or packed column or a gas scrubber.

Optionally, the medium of the H<sub>2</sub>S removal zone is buffered. Preferred buffering compounds are carbonates, bicarbonates phosphates and mixtures thereof, especially sodium carbonate and/or sodium bicarbonate. The concentration of the buffering compounds depends inter alia on the composition of the gas flow and is generally adjusted in such a way, that the pH of the reaction medium in the H<sub>2</sub>S removal zone is between 5.5 and 10, more preferably between 6.5 and 9.

In step (e) of the process according to the invention the hydrogen-sulphide-comprising aqueous stream obtained in step (d) is contacted with sulphide-oxidizing bacteria in the presence of oxygen in a oxidation reactor to obtain a sulphur slurry and a regenerated aqueous alkaline washing liquid. The main reaction that can take place in the oxidation reactor in step (e) is the microbiological formation of sulphur and sulphate:

(12) Sulphur production  $HS^- + \frac{1}{2} O_2 \rightarrow 1/8 S_8 + OH^-$ 

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(13) Sulfate production  $HS^- + 2O_2 + OH^- \rightarrow SO_4^{2-} + H_2O$ 

The term sulphur slurry as used herein refers to a slurry comprising one or more products of the main reactions, including reactions (12) and (13), that can take place in the oxidation reactor.

The term regenerated aqueous alkaline solvent as used herein refers to an aqueous alkaline solvent wherein at most 2 w/w% impurities are present, preferably at most 1 w/w%.

Reference herein to sulphide-oxidizing bacteria is to bacteria which can oxidize sulphide to elemental sulphur. Suitable sulphide-oxidizing bacteria can be selected for instance from the known auto tropic aerobic cultures of the genera Thiobacillus and Thiomicrospira.

Typical pressures in the oxidation reactor in step (e) are between 1 and 2 bara.

Suitably, the oxidation reactor has a volume of between 5 and 2500  $\ensuremath{\text{m}^3}$ , preferably between 10 and 2000  $\ensuremath{\text{m}^3}$ .

Preferably, the reaction medium in the oxidation reactor in step (e) is buffered. The buffering compounds are chosen in such a way that the bacteria present in the oxidation reactor tolerate them. Preferred buffering compounds are carbonates, bicarbonates phosphates and mixtures thereof, especially sodium carbonate and/or sodium bicarbonate. The concentration of the buffering compounds depends inter alia on the composition of the gas flow and is generally adjusted in such a way, that

the pH of the reaction medium in the oxidation reactor is between 5 and 10, more preferably between 6 and 8.

In step (f) of the process according to the invention at least part of the aqueous sulphur slurry obtained in step (e) is separated from the regenerated aqueous alkaline solvent. The phrase "at least part of" as used herein is to indicate that between 1 and 100%, preferably between 5 and 95 w/w%, more preferably between 10 and 90 w/w% of the sulphur is separated, based on the total weight of the slurry.

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Suitably, the separating step takes place in a solid/liquid separator. Suitable solid/liquid separators are described in Perry's Chemical Engineers' Handbook, 7th edition, section 22 (1997).

Typically, the sulphur content of the separated aqueous sulphur slurry is between 5 w/w% and 50 w/w%, based on the slurry. Typically, the water of the sulphur slurry is removed to an extent that a sulphur cake with a dry solids content of between 55 and 70% is obtained. Typically, the sulphur purity of the sulphur cake is between 90 and 98 w/w%, based on the total weight of the sulphur cake. Optionally, the sulphur slurry obtained in step (c) can be re-slurried, filtered and dried to obtain a sulphur paste with a purity of at least 95 wt% sulphur, preferably at least 99 wt% sulphur. The sulphur paste thus-obtained can optionally be dried to produce a powder with a dry weight content of at least 85%, preferably at least 90%. This powder can suitably be applied as a fungicide or as a miticide.

The sulphur produced in the process according to the invention has a hydrophilic nature and does not cause the fouling problems that are typically caused by sulphur produced by non-biological liquid processes. Another

advantage of the sulphur produced in the process according to the invention is that it is very suitable for use as a fertilizer.

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In step (g) of the process according to the invention, regenerated aqueous alkaline washing liquid obtained in step (e) is recycled to the H<sub>2</sub>S-removal zone in step (d). Suitably, between 10 and 99%, preferably between 30 and 95%, more preferably between 40 and 90% of the total amount of regenerated aqueous alkaline washing liquid obtained in step (e) is recycled to the H<sub>2</sub>S-removal zone in step (d). By recycling the regenerated aqueous washing liquid to the H<sub>2</sub>S-removal zone fresh aqueous washing liquid is supplied to the H<sub>2</sub>S-removal zone for the removal of H<sub>2</sub>S. This enhances the removal of H<sub>2</sub>S to a concentration of 30 ppmv or less, suitably 20 ppmv or less, preferably 10 ppmv or less.

The process according to the invention is especially suitable for the treatment of a gaseous CO-containing stream, especially a syngas stream, an offgas stream from a carbon black plant, or a refinery gas stream. Syngas is a general term that is applied to mixtures of inert components, carbon monoxide, carbon dioxide and hydrogen that are derived from the gasification of coal, oil residues, waste or biomass. The main components of syngas are hydrogen and carbon monoxide. Further, often carbon dioxide and traces of methane are present. Refinery streams concern crude oil derived gaseous streams containing smaller or larger amounts of sulphur compounds. Recycle streams and bleed streams of hydrotreatment processes, especially hydrodesulfurisation processes, can also suitably be treated by the process according to the invention.

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The invention will now be illustrated by means of schematic figure 1. Figure 1 depicts a typical process scheme according to the invention, wherein a gas stream comprising SO2, HCN, H2S and optionally COS, CS2 and NH3 enters the hydrogenation zone (2) via line (1) and is contacted with the hydrogenation catalyst to remove the SO2. After treatment in the hydrogenation zone the second gas stream, which is SO2-depleted, leaves the hydrogenation zone via line (3) and enters the hydrolysis zone (4) where it is contacted with a hydrolysis catalyst to remove HCN and optionally COS and/or CS2. Optionally, steam or a steam/water mixture can be added to the hydrolysis zone via line (25). After treatment in the hydrolysis zone, the third gas stream, which is depleted of HCN, COS and/or CS2, leaves the hydrolysis zone via line (5) and enters the  $HN_3$ -removal zone (6), where it is treated with aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream. After treatment in the NH3-removal zone, the fourth gas stream, which is depleted of HCN, COS and/or  $CS_2$  and  $NH_3$ , leaves the  $HN_3$ -removal zone via line (7) and enters the  $H_2S$ -removal zone (8), where it is contacted with an aqueous washing liquid. The H2S-depleted gas stream is led from the  $H_2S$ -removal zone via line (9), optionally via a knockout vessel (10) and can be further processed via line (11). A sulphide-comprising aqueous stream leaves the  $H_2S$ -removal zone via line (12) and enters a flash vessel (13).  $H_2S$ -depleted excess gas is vented off from the flash vessel through line (14). In the case that flash gas contains some  $H_2S$ , the  $H_2S$  needs to be removed in a small flash gas contactor before

further use as fuel gas. The sulphide-comprising aqueous stream is led via line (15) to the aerobic reactor (16) where the sulphide compounds are oxidized. Nutrients and air are fed to the aerobic reactor via feed lines (17) and (18). The containing-containing solid/liquid mixture generated in the aerobic reactor is led via line (19) to a solid/liquid separator (20) where the solid containing is separated and discharged via line (21). The liquid is led back to the bioreactor via line (22). Off-gas is vented from the aerobic reactor via line (23). The regenerated aqueous alkaline solvent is led to the H<sub>2</sub>S-removal zone via line (24).

The invention will now be illustrated by the following non-limiting examples.

## 15 EXAMPLE 1 (comparative)

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A gas stream containing containing compounds and HCN with concentrations as given in table 1 is heated to a temperature of 280 °C and led to a reactor filled with a stacked bed of hydrogenation catalyst and hydrolysis catalyst. The gas is cooled in a quench tower at 40 °C and treated in an amine/Claus unit to remove the H<sub>2</sub>S. The concentrations of containing compounds and of HCN in the treated gas is given in table 1.

Table 1

	Gas to treating	Gas after treating
	system (v/v%)	system (v/v%)
H <sub>2</sub> O	6.7	3.2
H <sub>2</sub> S	1.9	0.01
so <sub>2</sub>	0.1	0.05
CS <sub>2</sub>	0.09	0.01
cos	0.28	0.01
HCN	0.03	0.01
NH3	0.04	0.03

#### EXAMPLE 2 (according to the invention)

A gas stream containing containing compounds and HCN with concentrations as given in table 2 is heated to a temperature of 280 °C and led to a reactor filled with a stacked bed of hydrogenation catalyst and hydrolysis catalyst. The gas is cooled in a quench tower at 40 °C, treated in an NH3-scrubber and subsequently treated in a H2S-removal unit, followed by oxidation of the resulting hydrogensulphides in a bioreactor according to the invention. The concentrations of the containing compounds and of the HCN in the treated gas is given in table 2.

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Table 2

	Gas to treating	Gas after treating
	system (v/v%)	system (v/v%)
H <sub>2</sub> O	40	6.8
H <sub>2</sub> S	0.9	0.0002
so <sub>2</sub>	0.1	0.001
cs <sub>2</sub> ·	0.04	0.0002
cos	0.01	0.001
HCN	0.1	0.001
NH3	0.03	0.001

From the examples it is clear that with the process according to the invention a substantially lower concentration of containing compounds, especially of H<sub>2</sub>S, SO<sub>2</sub>, CS<sub>2</sub> and COS is achieved, while the concentration of HCN is also lowered.



#### CLAIMS

- 1. A process for the removal of  $SO_2$ , HCN and  $H_2S$  and optionally one or more compounds from the group of  $COS_2$  and  $NH_3$  from a first gas stream, which process comprises the steps of:
- (a) removing SO<sub>2</sub> from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;

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- (b) removing HCN and optionally COS and/or CS2 from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;
- (c) removing NH<sub>3</sub> from the third gas stream by contacting the third gas stream in a NH<sub>3</sub>-removal zone with an aqueous acidic washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream;
- (d) removing  $H_2S$  from the fourth gas stream by contacting the fourth gas stream in a  $H_2S$ -removal zone with an aqueous alkaline washing liquid to obtain a  $H_2S$ -depleted gas stream and a hydrogensulphide-comprising aqueous stream;
- (e) contacting the hydrogensulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in an oxidation reactor to obtain a containing slurry and a regenerated aqueous alkaline washing liquid;
- (f) separating at least part of the containing slurry obtained in step (e) from the regenerated aqueous alkaline washing liquid and;

- (g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the  $H_2S$ -removal zone in step (d).
- 2. A process according to claim 1, wherein the containing load in the  $H_2S$ -removal zone in step (d) is between 50 and 50000 kg/day, preferably between 75 and 20000 kg/day, more preferably between 100 and 10000 kg/day.

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- 3. A process according to claim 1 or 2, wherein the total concentration of containing compounds in the treated gas, especially  $H_2S$ , is below 30 ppmv, preferably between between 0.01 and 20 ppmv.
- 4. A process according to any of claims 1 to 3, wherein the washing liquid in step (d) is buffered, preferably at a pH of between 5.5 and 10, more preferably at a pH between 6.5 and 9.
- 5. A process according to any of claims 1 to 4, wherein the contents of the oxidation reactor in step (e) is buffered, preferably at a pH between 5 and 10, more preferably between 6 and 8.
- 6. A process according to any of claims 1 to 5, wherein the oxidation reactor in step (e) has a volume of between 5 and  $2500 \text{ m}^3$ .
  - 7. A process according to any of claims 1 to 6, wherein the containing slurry obtained in step (e) is resolutried, filtered and dried to obtain a purity of at least 95 wt% containing, preferably at least 99 wt% containing.
- 8. A process according to any of claims 1 to 7, wherein water or steam or a mixture thereof is added to the second gas stream prior to contacting the first gas stream in a hydrolysis zone with a hydrolysis catalyst in step (b).

9. A process according to claim 8, wherein the amount of water/steam added is such that the water/steam content of the second gas stream is between 10 v/v% and 80 v/v%, preferably between 20 v/v% and 70 v/v%, more preferably between 30 v/v% and 50 v/v%, based on steam%.

#### ABSTRACT

A PROCESS FOR THE REMOVAL OF  ${\rm SO_2}$ , HCN AND  ${\rm H_2S}$  AND OPTIONALLY COS,  ${\rm CS_2}$  AND  ${\rm NH_3}$  FROM A GAS STREAM

The invention relates to a process for the removal of  $SO_2$ , HCN and  $H_2S$  and optionally one or more compounds from the group of COS,  $CS_2$  and  $NH_3$  from a first gas stream, which process comprises the steps of:

- (a) removing SO<sub>2</sub> from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;
- (b) removing HCN and optionally COS and/or  $CS_2$  from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;
- (c) removing NH<sub>3</sub> from the third gas stream by contacting the third gas stream in a NH<sub>3</sub>-removal zone with an aqueous acidic washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream;
- (d) removing  $H_2S$  from the fourth gas stream by contacting the fourth gas stream in a  $H_2S$ -removal zone with an aqueous alkaline washing liquid to obtain a  $H_2S$ -depleted gas stream and a hydrogensulphide-comprising aqueous stream;
- (e) contacting the hydrogensulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in a oxidation reactor

to obtain a containing slurry and a regenerated aqueous alkaline washing liquid;

- (f) separating at least part of the containing slurry obtained in step (e) from the regenerated aqueous alkaline washing liquid and;
- (g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the  $H_2S$ -removal zone in step (d).

(Fig.)

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